

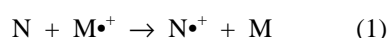
Spectroscopic Detection and Kinetic Analysis of Short-Lived Aromatic Cation Radical Using an Electron Transfer Stopped-Flow Method

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In the electrochemical oxidation of aromatic molecules in aprotic solvents, the cation radicals are formed as a result of one-electron transfer. If such cation radicals are short-lived, the spectroscopic detection should be very difficult due to the consecutive reactions. In addition, the heterogeneous natures of the electrode reaction would hinder the observation of pure absorption spectra of the cation radicals.

In the present paper, I would like to present an electron transfer stopped-flow (ETSF) method as a new methodology for the spectroscopic observation and the kinetic analysis of the short-lived intermediates. The principle of the ETSF method has been described previously [1]. In this method, for a concrete example, unstable cation radicals ($N^{\bullet+}$) are formed via the electron transfer with stable cation radicals ($M^{\bullet+}$). That is, when the oxidation potential of the $M^{\bullet+}/M$ couple is positive to that of the $N^{\bullet+}/N$ couple, the electron transfer reaction of Eq. 1 should be favorable thermodynamically.



Thus, by mixing the solutions of N and $M^{\bullet+}$, we can form $N^{\bullet+}$ via. Eq. 1 and initiate the reaction of $N^{\bullet+}$.

Such a formation of cation radicals by the other cation radicals is well-known, and the correlation between the redox equilibria and the potentials have been investigated previously. Nevertheless, it can be emphasized that, by combining the electron transfer reactions with a stopped-flow operation, spectroscopic measurements for short-lived intermediates which have never been investigated would become possible, in particular, with a help of the recent development of rapid-scan spectrophotometer.

In our previous work [1], as a substrate to form stable cation radicals, $M^{\bullet+}$, in Eq. 1, we used tris(4-bromophenyl)amine (TBPA), which is known to form the very stable cation radical in AN due to the bromo-substituents that work concurrently to make the oxidation potential positive to that of triphenylamine. However, for the formation of $N^{\bullet+}$ in Eq. 1, the higher oxidation potential of the $M^{\bullet+}/M$ couple should be desirable because the targeted molecules, N , can be expended. Thus, in the present work, tris(2,4-dibromophenyl)amine (TDBPA), which has further higher oxidation potential than TBPA, was used as a substrate to form $M^{\bullet+}$.

Using $TDBPA^{\bullet+}$, the formation of anthracene derivative cation radicals in acetonitrile (AN) was first examined. By simply mixing an AN solution of $TDBPA^{\bullet+}$ with an AN solution containing anthracene derivatives, the anthracene derivative cation radicals can be generated for several derivatives. Indeed, the absorption spectra of anthracene and 9-methylantracene cation radicals can be detected in spite of very rapid decay

of the cation radicals. Compared with the se derivatives, 9-bromo- and 9-phenylantracene cation radicals are much more stable, so that the nucleophilic reactions of these cation radicals were analyzed. In actual, the kinetic process can be observed by mixing an AN solution of $TDBPA^{\bullet+}$ with an AN solution containing both anthracene derivatives and nucleophiles. Fig.1 shows the dynamic transformation of absorption spectra of 9-bromoanthracene cation radical in the reaction with 50 mM methanol. By analyzing the decay profile, the kinetic analysis could be carried out successfully, and the changes in the reactivity due to the substituents was clarified.

As another example, the formation of pyrene cation radical was examined using the ETSF method. While perylene cation radical is so stable that the nucleophilic reaction were analyzed previously, the spectroscopic observation of pyrene cation radical has been difficult. However, in the ETSF method, by mixing an AN solution of $TDBPA^{\bullet+}$ with an AN solution of pyrene, the absorption spectrum of pyrene cation radical could be detected as shown in Fig. 2, though the decay was very rapid as shown in Fig.2.

The details of these spectroscopic observation and kinetic analysis of the short-lived cation radicals will be presented at the meeting.

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[1] M. Oyama et al., *Electrochem. Commun.*, 2000, **2**, 675.

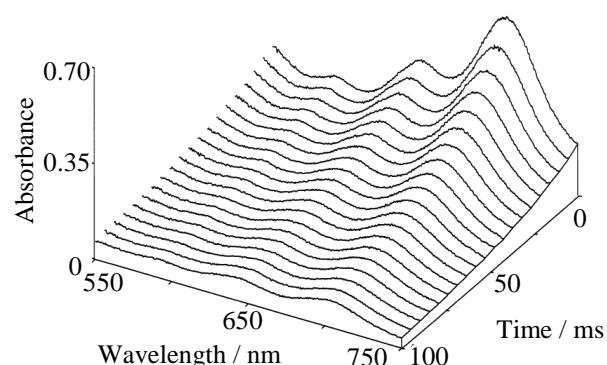


Fig.1. Absorption spectra of 9-bromophenylantracene cation radical in the reaction with 50 mM methanol

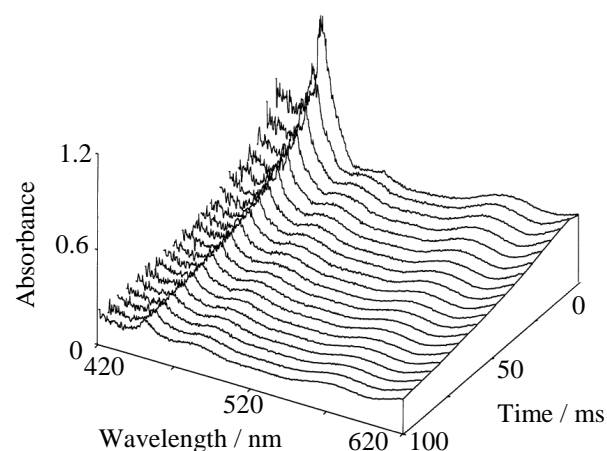


Fig.2. Absorption spectra of pyrene cation radical